

DRAWINGS ATTACHED

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(54) IMPROVEMENTS IN CONTROL METHOD AND
 APPARATUS FOR CONTROLLING METALLURGICAL
 PROCESSES IN OXYGEN BEARING ATMOSPHERE

(71) We GENERAL ELECTRIC COMPANY, a Corporation organised and existing under the laws of the State of New York, United States of America, of 1 River Road, Schenectady, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Background of Invention

Field of Invention

This invention relates to a new and improved method and apparatus for controlling metallurgical and chemical processes carried out in oxygen bearing atmospheres.

More specifically, the invention relates to a control method and apparatus for controlling the processing of the products in oxygen bearing gaseous atmospheres by determining the ability of the oxygen in the gas phase to chemically affect the product through reduction, oxidation, etc., and thereafter employ this determination in the further control of the conditioning of the gaseous atmosphere in order to optimize its processing capability.

Description of Prior Art

The oxygen content in oxygen bearing gaseous atmospheres (termed the gas phase) employed in industrial processes greatly affects the product being produced by the process. Whether or not the gas phase oxygen will react with the product depends upon the oxygen potential of the gas phase oxygen, the temperature, and the nature of the product being produced. Knowing these factors, the ability of the gas phase oxygen to react (oxygen potential) can be regulated so that it will have the most desirable (optimized) effect upon the product.

The procedure commonly used at present in most industrial processes is to correlate the ability of the oxygen in the gas phase to react with the product by measuring one

or more of the other components in the gaseous atmosphere employed in a process in question. These indirect measurements are then used to regulate the oxygen potential of the gaseous atmosphere. The use of dew-point, CO and/or CO₂ measurements of furnace atmospheres during the treating of metals are primary examples of these known commonly used procedures. The inherent inaccuracies of this type of indirect measurement procedures makes the close control of the oxygen potential in such gaseous atmospheres extremely difficult. The direct measurement of the oxygen potential of a gaseous atmosphere employed in industrial processes, is far superior to the methods presently in use in that it allows a much better control of the process than presently can be obtained.

In practicing the invention, a control method and apparatus is provided for controlling metallurgical and chemical processing of a product in a controllable processing vessel having a gaseous atmosphere containing oxygen. In practicing the invention a source of process control gas is provided along with control means for controlling the supply of the process control gas from the source to the processing vessel. Measurement means are provided for directly sensing the oxygen potential of the gaseous atmosphere in the vessel and deriving output measurement signals indicative of the oxygen potential. The output measurement signals are then supplied through feedback and control means to control the supply of process control gas to the processing vessel for optimizing the metallurgical process. In preferred embodiments of the invention, the oxygen potential of the gaseous atmosphere is measured by a gas analyzer of the type capable of obtaining a direct measurement of the equilibrium oxygen partial pressure of the gaseous atmosphere in the vessel to thereby provide an indication of the oxygen potential of the gaseous atmosphere.

In accordance with certain specific examples of the invention, the product being processed may be a metal product which is being either reduced or oxidized and with respect to which the equilibrium oxygen partial pressure at which the metal begins to reduce or oxidize is given by the expression

$$\Delta pO^{\circ}_{MaOb} = \frac{(\Delta G^{\circ}_{MaOb})/b}{4.575 T}$$

where the process being controlled is one for oxidizing a metal product, the control gas flow rate is regulated so that

$$pO < pO^{\circ}_{MaOb}$$

and where the process is one for reducing a metal oxide, the control gas flow rate is regulated to that

$$pO > pO^{\circ}_{MaOb}$$

Other features and many of the attendant advantages of this invention will be appreciated more readily as the same becomes better understood by reference to the following detailed description, when considered in connection with the accompanying drawings, wherein like parts in each of the several figures are identified by the same reference character, and wherein:

FIGURE 1 is a schematic drawing of oxygen in the gas phase and oxygen in the product, and the manner in which they interact;

FIGURE 2 is a functional block diagram of a control apparatus for a protective atmosphere control employing an annealing furnace for annealing metal articles;

FIGURE 3 is a profile of the H_2O/H_2 ratio in a continuous annealing furnace obtained through the direct measurement of the gas phase oxygen partial pressure;

FIGURE 4 is a functional block diagram of a direct reduction process control constructed in accordance with the invention;

FIGURE 5 is a functional block diagram of a sintering atmosphere control constructed in accordance with the invention;

FIGURE 6 is a functional block diagram of a carburizing atmosphere control constructed in accordance with the invention; and

FIGURES 7 and 8 are graphs of the computed properties of an atmosphere generator output versus carbon depletion characteristics and versus the air/fuel ratio characteristic, respectively, for a carburizing control of the type shown in FIGURE 6.

Detailed Description of Preferred Embodiments

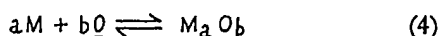
Control philosophy

As stated above, oxygen is involved in one way or another in a large number of industrial processes. The continuous measurement of the oxygen partial pressure in the gases involved in these processes accordingly yields valuable information for use in control of the processes. FIGURE 1 of the drawings is a schematic drawing of the interaction between the gas phase oxygen and a metal product being processed. The oxygen in the gas phase will attempt to come into equilibrium with the oxygen in the product according to the following relations:



$$K_1 = P_{O_2} / \alpha_O^2 \quad (2)$$

$$P_{O_2} / K_1 = \alpha_O^2 = [\alpha_{C_O}]^2 \quad (3)$$



$$K_2 = \frac{\alpha_{MaOb}}{\alpha_M \alpha_O^b} \quad (5)$$

where

O_2 = oxygen in the gas phase

O = Oxygen in the metal phase

P_{O_2} = oxygen partial pressure in the gas

phase

α_O = the activity of oxygen in the metal

phase

γ = the activity coefficient of oxygen in the

metal phase

C_O = the concentration of oxygen in the

metal phase

K_1 = equilibrium constant of reaction 1

K_2 = equilibrium constant for reaction 5

α_M = the activity of metal in the metallic phase

α_{MaOb} = activity of oxide in the oxide phase

$MaOb$ = stoichiometric oxide formula

a, b, c = stoichiometric coefficients for the reaction

As can be seen from the above relationships, the partial pressure of the oxygen in the gas phase is directly related to the oxygen content in a product being processed in an oxygen bearing gaseous atmosphere. In systems where metals are involved, the oxygen partial pressure also affects the type and rate of formation of metal oxides. By measuring the gas phase oxygen partial pressure, and knowing the product's temperature and chemical affinity for oxygen, the ability of the oxygen in the gas phase to affect the product can be determined and controlled.

Measurement of Gas Phase Partial Pressure
Electrochemical cells for the measurement of thermodynamic quantities or compositions, as a result of recent developments, may now be applied in practical systems for directly measuring the equilibrium oxygen partial pressure of gaseous atmospheres for use in controlling industrial processes at extremely high temperatures (in the neighborhood of 1000°C). The Instrument Department of the General Electric Company has recently introduced for sale in its line of commercial instruments an "Oxysensor" unit suitable for this purpose. The "Oxysensor" unit is an oxygen concentration cell consisting of stabilized zirconia electrolyte having electrodes attached to two opposite surfaces that can be exposed to different oxygen pressures. The closed-end tube configuration of the electrolyte makes it especially convenient to expose the inner-reference electrode to a known reference gas, such as air, having a known oxygen partial pressure. An electrical potential (volts) will be developed between the two electrodes immersed in two gases having different oxygen partial pressures; the gases being separated by an oxygen-ion conducting, calcium-stabilized, zirconium oxide electrolyte. The measured open cell voltage is related to the oxygen partial pressure in the two gases by the Nernst equation.

The Nernst equation states that "the open cell voltage is proportional to the quantity $\frac{RT}{4F}$

multiplied by the natural log of the ratio of the oxygen partial pressure in the two gases," and may be written as

$$V_0 = \left(\frac{RT}{4F} \right) \ln \left(\frac{P_{O_2}}{P'_{O_2}} \right)$$

where R is the gas constant, T is the absolute temperature in °K, F is the Faraday's constant, P_{O_2} is the partial pressure of the gas the P'_{O_2} is the partial pressure of the reference gas.

In operation, the temperature of the "Oxysensor" is preset and the oxygen partial pressure in the reference gas is known. Therefore, by measuring the open cell voltage between the two gases, the oxygen partial pressure in the gaseous atmosphere being monitored can be calculated by the Nernst equation. This measured oxygen partial pressure (P_{O_2}) is directly related to the oxygen concentration and chemical composition of the gas being measured. The General Electric "Oxysensor" has been designed to operate, with a minimum of filtering necessary, on industrial gas samples. The "Oxysensor" includes its own filters, dryers and pump for gas preparation. A needle valve and gas flow meter is also

included for regulating and measuring the gas flow rate. The "Oxysensor's" temperature is maintained at 850°C, plus or minus 5°C, by a suitable solid-state proportional controller. The "Oxysensor's" voltage output is treated in a self-contained amplifier circuit so that it can be read directly as a pO value on a gauge, or it may be outputted to subsequent instrumentation such as a recorder or computer. The value pO is related to the measured equilibrium oxygen partial pressure value P_{O_2} by the expression

$$pO = \log \left(\frac{1}{[P_{O_2}]^{1/2}} \right) \quad (6)$$

The characteristics of the General Electric "Oxysensor" are such that it is capable of continuously indicating the oxygen potential of gaseous media employed in industrial processing, and possesses the following desirable characteristics:

- (a) logarithmically increasing signal with linearly decreasing oxygen partial pressure
- (b) extremely low drift
- (c) continuous fast response (within five seconds)
- (d) corrosive and particle laden gas streams can be passed through the instrument without adversely affecting the instrument's sensitivity

Requirements for Composition Measurement of Gases Used in Industrial Applications

A fundamental question relevant to obtaining composition measurement of gases employed in industrial processes for use in the further control of the processes, is how many independent measurements are required, at a given temperature and total pressure, to be able to derive a reliable indicia for use in the control. The phase rule of thermodynamics states that the minimum number of independent measurements that is required to completely specify the composition of a gas sample, is one less than the number of components (elements) in the gas under consideration. However, for the control of many processes it is not required to completely specify the composition of the gas being measured. A question relevant to composition measurements, or in connection with a particular type of gas, is what aspect of the composition is important and how will it be used. The answers to this question tend to fall into two general categories: (1) situations where the composition itself is important, in order to obtain a measurement of the change in the amount of a particular component or species in a gas process; and (2) situations where the

gas composition is used to measure some more abstract property of the gas, generally by computing or substituting into a formula. Either of these cases may require less than the minimum number of independent measurements required to completely establish the composition.

When the oxygen content in a processing gas is above approximately 0.1 percent, the other species present in the gas act as diluents. Paramagnetic oxygen sensors and combustion meters have been used commonly to control processes with this level of oxygen. Only recently has the "Oxysensor" concept been utilized in connection with processes of this nature where its logarithmic response, as well as its insensitivity to solid particles in the gas phase, make it an extremely useful instrument. In this category, the "Oxysensor" has been used successfully in controlling a BOF process in series with other instruments to allow calculation of the way lance oxygen is utilized in this particular oxidation process.

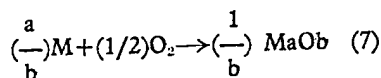
The "Oxysensor" also is very well suited to the determination of the stoichiometric combustion point (S.C.P.). The drastic change in the equilibrium oxygen partial pressure of combustion products as the air/fuel ratio is varied through the S.C.P., leads to a step-function-like change in the output of the "Oxysensor". The S.C.P. is a very good example of how one particular characteristic of a multi-component gas composition can be determined by the "Oxysensor" without additional information required.

While it is extremely useful in the above-discussed situations, the "Oxysensor" really comes into its own when the free oxygen is less than 10^{-6} atmospheres where the other species in a gaseous composition usually determine, by reaction, the equilibrium oxygen partial pressure. Measurement of the other species of the gas phase (such as CO, CO₂, H₂O, and H₂) have been used in the past and presently are being used for control purposes. Combinations of these measured or assumed species concentrations are utilized to show the ability of the gas phase to effect a product being produced (oxidized, reduced, and carburized). The assumption made in connection with controls of this type, however, is that the gas is at or near equilibrium so that thermodynamic relationships hold. Dew-point, infra-red and paramagnetic instruments do not cause the gas sample to attain equilibrium at an explicitly known temperature as does the "Oxysensor". Therefore, the use of the above-listed known types of sensors are all based on an assumption that does not apply to the "Oxysensor". In many cases measurements made by such instruments are being used to indirectly determine the oxygen partial pressure of the gas through use of suitable reaction equations. For these applications, the "Oxysensor" could be and

should be used since it measures the equilibrium oxygen partial pressure directly under known temperature and pressure conditions. The equilibrium oxygen partial pressure is also a thermodynamically meaningful quantity.

Control Theory

One reason for the utility of the logarithmic response of the "Oxysensor" is the compatibility of its output signal with the form of the general reaction equation expressing the oxidation of a metal by oxygen:



where both the metal M and its oxide MaOb are either solid or liquid.

The oxide in reaction (7) will have an associated standard Gibbs free energy of formation, per mole of oxide,

$$\Delta G^\circ_{MaOb}$$

A negative value for this factor indicates a stable oxide, and the greater the magnitude of

$$\Delta G^\circ_{MaOb}$$

the more stable the oxide. Values of

$$\Delta G^\circ_{MaOb}$$

have been exclusively calculated and tabulated (plotted) against temperature, and appear in the literature in the form of Ellingham diagrams. The generalized pO value corresponding to the oxygen partial pressure that would result from reaction (7) is given by the following equation:

$$pO^\circ_{MaOb} = \frac{(\Delta G^\circ_{MaOb})/b}{4.575T} \quad (8)$$

where

$$\Delta G^\circ_{MaOb}$$

is expressed in cal/mole.

The oxide MaOb will tend to be reduced if

$$pO > pO^\circ_{MaOb} \quad (9)$$

and conversely, the metal M will be oxidized if

$$pO < pO^\circ_{MaOb} \quad (10)$$

Control Implementation—Protective Atmosphere Control

Annealing of metal products under protective atmospheres is a prime example of the manner in which, prior to the "Oxysensor", indirect measurements were used to determine the oxygen partial pressure of an atmosphere. Until the advent of the "Oxysensor", instruments were not available to measure down to 10^{-27} atmospheres oxygen (equivalent dewpoint of minus 80°F.) as required for applications such as the bright annealing of stainless steel strip. However, with the "Oxysensor" such applications are entirely feasible. Whether a metal product being annealed will be oxidized is a direct function of the protective atmosphere equilibrium oxygen partial pressure. The equilibrium oxygen partial pressure, given in terms of pO, at which a metal would, according to thermodynamics, begin to oxidize, is set forth by equation (8). The gas flow rate of the gaseous atmosphere supplied to the annealing furnace should be regulated so that the relation set forth in equation (10) is maintained for those processing temperatures where reaction kinetics are not rate limiting the oxide formation.

FIGURE 2 of the drawings is a functional block diagram of an atmosphere control system suitable for use in controlling the operation of an annealing furnace shown at 11. The annealing furnace 11 is fired by a suitable fueling system whose operation is controlled by a controller 12 with the assistance of suitable processing temperature sensors shown at 13. The controller 12 may comprise an on-line, general purpose, digital process computer. The computer includes suitable analog-to-digital and digital-to-analog converters for converting input analog signals such as those obtained by the temperature sensors 13 into digital values for computation purposes, and for reconvertng output digital control signals derived by the computer into suitable analog signals for application to the fuel system controls to thereby control the temperature at which the annealing furnace 11 operates along several points in the length of the furnace. Such computer controlled temperature controlling arrangements are old and well known in the industry, and therefore will not be described in further detail.

In accordance with present invention, the annealing furnace 11 has a process control gas supplied to it at a number of points along its length from a suitable gas generator shown at 14. The gas generator 14 supplies to the annealing furnace at a number of points along its length a protective atmospheric control gas of known composition whose oxygen partial pressure is measured at the output of the gas generator and at several points along the length of the annealing furnace by pO sensor means 15 comprising an "Oxysensor".

The output of the "Oxysensor" is supplied to the control computer 12 for use by the computer in performing the computations required to maintain a protective gaseous atmosphere within the annealing furnace having a desired oxygen partial pressure at the several measured points. For this purpose, the system also includes gas flow rate measuring and control means shown at 16 for measuring and controlling the gas flow rate supplied to the several points along the length of the annealing furnace 11.

If desired, control by the computer over the composition of the gas supplied by the generator 14 may be obtained through the provision of an additional feedback and control loop indicated by the dotted lines 17 where such close control of the atmospheric composition, is required. For most applications, air will constitute a primary constituent of the protective atmosphere control gas supplied by the generator 14. With such arrangements, the feedback loop comprised by the dotted line 17 may be employed to control the relative amount of air being supplied to the gas generator 14 to thereby vary the composition of the gas. This control, together with the flow rate controls provided at each of the several points along the length of the annealing furnace by the gas flow rate measuring and control means 16 in conjunction with the "Oxysensor" means 15, makes available a protective atmosphere control system that is capable of extremely close control over the conditions at several points along the length of an annealing furnace. As stated above, the gas flow rate within the furnace would be closely regulated so that the relation set forth in equation (10) would be maintained.

FIGURE 3 of the drawings is a plot of an actual profile of the H_2O/H_2 ratio maintained in a continuous annealing furnace by a control system such as that shown in FIGURE 2 of the drawings. To obtain the data shown in FIGURE 3, "Oxysensors" monitored the oxygen partial pressure along the length of the furnace in order to diagnose those conditions (air-in-leakage, too high an oxygen partial pressure in the cooling zone, etc.) that cause strip oxidation. The output measurement signals derived at these several points may then be employed through the medium of the computer and its associated controls in the further control of the operation of the furnace to optimize the annealing process.

Direct Reduction

In a direct reduction process oxygen is taken out of an oxide and becomes part of the reducing gas, and is used in the recovery of certain metals. The ability of the reducing gas to extract oxygen is a direct function of the equilibrium oxygen partial pressure of

the gas. The oxygen extracted per unit of reducing gas used determines the reduction rate, and accordingly, the process efficiency. The process efficiency is defined as

$$\frac{pO_{in} - pO_{out}}{pO - pO_{MaOb}} \quad (11)$$

where pO_{in} is the oxygen potential of the recirculated gas supplied to a gas generator employed in providing reducing gas to the direct reduction vessel and pO_{out} is the oxygen potential of the output gas supplied from the gas generator. These measurements along with the flow rates and air/fuel ratio into the gas generator can be used to control the pO and flow rate of the processing gas to the direct reduction vessel, monitor the process efficiency and reduction rate, and control the amount of processing gas recycled and produced.

FIGURE 4 of the drawings is a functional block diagram of a direct reduction process control constructed in accordance with the invention. The control shown in FIGURE 4 is intended for use in controlling the operation of a direct reduction vessel shown at 21. The direct reduction vessel 21 is of the counter-flow type wherein oxide materials to be reduced are supplied to one end of the vessel (indicated by the arrow 22) and are taken out at the opposite end of the vessel (indicated by the arrow 23). A suitable reducing gas is supplied from a gas generator unit 24 to the end of the direct reduction vessel 21 from which the product being reduced is taken, and the exhausted or used reducing gas is removed from the vessel from its opposite end. A portion of such used gas is recirculated back through a connection shown at 25 to the gas generation unit for reuse, and another portion may be bled off and discarded as indicated at 26. As a consequence of this arrangement, it will be appreciated that the reducing gas flows counter to the flow of the oxide material being reduced through the direct reduction vessel 21. If desired, the portion of the reducing gas recirculated back to the gas generator 24 by connection 25 can be cleaned by suitable cleaning equipment disposed in the connection 25.

The gas generator 24 may be of any conventional type and preferably uses air (as indicated at 27) in the generation of the reducing gas supplied to vessel 21. The flow of air supplied to gas generator 24 is monitored and controlled by a suitable flow rate monitor and control means shown at 28 for maintaining a desired air/fuel ratio within the gas generator 24. The flow rate monitor and control means 28 is in turn controlled by a suitable control computer 12. The control computer 12 comprises a standard, on-line

digital process control computer having suitable D-A and A-D converters, and coacts processing temperature sensing means indicated at 13 for maintaining the temperature within the direct reduction vessel 21 at desired values.

In addition to the above components, the direct reduction process control of FIGURE 4 further includes oxygen partial pressure sensing and flow rate control means shown at 29 for sensing and controlling the oxygen partial pressure of the output process control gas (pO_{out}) supplied from the gas generator 24 to the direct reduction vessel 21, and for sensing and controlling the oxygen partial pressure of the portion of the recirculated reducing gases (pO_{in}) supplied through connection 25 from the output of the direct reduction vessel to the gas generator 24. The oxygen partial pressure sensing and flow rate control means 29 may comprise a General Electric "Oxysensor" together with suitable flow rate sensing and control valving systems for controlling the flow rate of the output process gas from generator 24 and the flow rate of the recirculated process gas through connection 25. If desired, a production rate monitor and control shown at 30 may be included in the system for monitoring and controlling the quality and output of the metallic products being produced in the direct reduction vessel 21.

In operation, the oxide material to be reduced is supplied at 22 to the reduction vessel 21 and is removed at 23. In travelling through the direct reduction vessel, the oxide material is exposed to the reducing action of the process control gases supplied from gas generator 24 and flowing through the direct reduction vessel 21 in a direction counter to the movement of the oxide material. The reducing reaction taking place in the direct reduction vessel, the reduction rate and accordingly the process efficiency of the system are defined by equation (11). By appropriately controlling the pO_{in} and the pO_{out} of the gases supplied to and from the gas generator unit 24, the reduction process taking place can be optimized.

Sintering Atmosphere Controls

The sintering of metals with more than one oxide polymorphic to obtain a specific oxide requires close control of the sintering atmosphere equilibrium oxygen partial pressure. For example, assume that a sintering process is to produce the metal oxide $MaOb$ but not $MaO(b+2c)$. The chemical relationship between these two oxides of the same metal is given by the expression



The equilibrium oxygen partial pressure of the sintering atmosphere in terms of pO has

to be maintained in a manner so as to satisfy the following relation:

$$pO^{\circ}_{\text{MaOb}} > pO > pO^{\circ}_{\text{MaO}(b+2c)} \quad (13)$$

To obtain this desired pO value, the flow rate and the pO of the processing gas into the sintering furnace must be measured and controlled.

FIGURE 5 of the drawings is a functional block diagram of a suitable sintering atmosphere control constructed in accordance with the invention for exercising the type of close required. The control shown in FIGURE 5 is employed in conjunction with a sintering furnace 31 of the type for use in carrying out the following reaction:



In performing the sintering reaction depicted by equation (14) the sintering furnace 31 is maintained at a suitable temperature through the medium of a processing temperature sensing and control system 13 operating in conjunction with a control computer 12. In addition, the sintering furnace 31 has supplied thereto a suitable process control gas from a gas generator 32. The process control gas supplied from the generator 32 is in part recirculated through a connection 33, with the recirculated portion of the process control gas being mixed with an appropriate primary gas (such as air) within the gas generator and supplied to the input of the sintering furnace. To control the composition of the process control gas supplied from the gas generator 32 to the furnace 31, suitable flow rate measuring and control means shown at 34 are provided which in turn are controlled by the computer 12. The flow rate measuring and control means 34 serves to adjust the air/fuel ratio of the gas generator 32 so as to optimize the composition of the process control gas being supplied to the sintering furnace 31. For this purpose, gas analyzer and flow rate control means shown at 35 are provided. The gas analyzer and flow rate control means 35 comprise "Oxysensor" units for deriving a measurement of the oxygen partial pressure of the portion of the sintering gases being recirculated through the connection 33 to the gas generator 32, and for sensing the oxygen partial pressure of the output control gas being supplied from the gas generator 32 to the sintering furnace. These sensed oxygen partial pressure measurement signals are then supplied to the control computer 12 which thereafter adjusts the flow rate of the recirculated sintering gases and the flow rate of the output control process gas from gas generator 32 to the furnace so as to optimize the sintering atmospheric conditions within the sintering furnace 31 in

accordance with the relation set forth in equation (13).

Carburizing Atmospheric Control

In gas carburizing of metal parts, the objective is to obtain a carbon concentration profile of a certain depth with a fixed surface carbon concentration. The generation of a carburizing atmosphere to do this requires the burning of a hydrocarbon fuel and the conditioning of the combustion products (drying and scrubbing) to obtain a gas of specified carbon potential. The gas equilibrium oxygen partial pressure is a function of the producing variables, i.e., fuel stoichiometry, air/fuel ratio, drying and scrubbing efficiencies, and carburizing load. By measuring the equilibrium oxygen partial pressure after each conditioning step, control of the gas carbon potential is obtained.

FIGURE 6 is a functional block diagram of a control system for the control of gas generation, conditioning and utilization in a carburizing furnace. In FIGURE 6, the carburizing furnace is shown at 41, and has supplied thereto a suitable carburizing gaseous atmosphere obtained from a gas generator shown at 42 and supplied to the carburizing furnace 41 through suitable drying and scrubbing equipments shown at 43 and 44. As stated above, the gas generator 42 burns a hydrocarbon fuel and supplies its products of combustion through the dryer and scrubber to the carburizing furnace 41. To control the burning of the hydrocarbon fuel, a suitable flow rate measurement and control unit shown at 45 is provided which in turn is controlled by an on-line, general purpose, digital process control computer 12. The computer 12 also controls the operation of the drying equipment 43 through a conventional dryer operation sensor and control unit 46, and controls the scrubbing equipment 44 through scrubbing equipment control 47 of known construction. Measurements of the oxygen partial pressure of the carburizing gas atmosphere are obtained at each of the outputs of the gas generator 42, the dryer 43 and the scrubber 44 by oxygen partial pressure measuring units 48, 49, and 51, respectively. The oxygen partial pressure measuring units 48—51 comprise General Electric "Oxysensor" units for measuring the equilibrium oxygen partial pressure after each conditioning step so as to control the gas carbon potential of the carburizing gases supplied to the carburizing furnace 41. In addition, a gas analyzing and processing temperature sensing and control means shown at 52 is provided for measuring the equilibrium oxygen partial pressure of the gaseous atmosphere in carburizing furnace 41 and supplying the same to the control computer 12. Unit 52 also serves to sense and control the temperature within the carburizing furnace 41 through the

medium of the control computer 12 in a conventional manner.

In operation, the carburizing control system shown in FIGURE 6 serves to generate and control the carburizing atmospheric gases supplied to the carburizing furnace 41 for obtaining a specific carbon potential. This is achieved by measuring the equilibrium oxygen partial pressure at the output of each stage of the development of the carburizing gas and appropriately controlling such stage so as to optimize the carbon potential of the gas. For this purpose, the range of oxygen partial pressures encountered may be from 10^{-12} to 10^{-20} atmospheres, and hence the "Oxysensor" is ideally suited for the implementation of a control system such as that shown in FIGURE 6.

FIGURE 7 of the drawings is a plot of the computed properties of the output from a carburizing atmosphere generator (comprised of the gas generator, dryer and scrubber) versus the carbon depletion and carbon activity in the furnace. In FIGURE 7 the gas carbon depletion is plotted as the abscissa with various other computed properties of the carburizing gas plotted as the ordinates. The curves shown in FIGURE 7 were obtained through digital computer simulation, and the computed properties plotted are the oxygen potential (pO and $\log P_{O_2}$)

in the left-hand margin, and the (A_c) carbon activity along the right-hand margin. From a consideration of FIGURE 7, it will be appreciated that the measurement of the equilibrium oxygen partial pressure of the carburizing atmosphere provides a direct indication of the carbon depletion and carbon activity characteristics of the carburizing gas atmosphere, and hence the carbon potential of the atmosphere.

FIGURE 8 of the drawings is a somewhat similar plot of other computed properties of a carburizing atmosphere showing the direct relation between the equilibrium oxygen partial pressure and the air/fuel ratio for use on the control of a carburizing gas generator (such as 42-44) of carburizing system shown in FIGURE 6.

In FIGURE 7, there are three upper lines indicating the gas in the dried state, as generated state and scrubbed state. Another set of identically marked lines appears in the lower portion of FIGURE 7, and, therefore, the solid lines also correspond to each other. However, the top three lines are to be read against the left-hand ordinate (either one, because the first scale from 5 to 10 represents pO , while the second scale from -10 to -20 represents the \log of P_{O_2}), while the bottom

three lines are to be read against the right-hand side ordinate which reads "carbon activated (A_c)". A_c is the chemical symbol for the

words carbon activated. The same situation exists between the three identified upper lines of FIGURE 8 with respect to the three unidentified lines at the bottom of FIGURE 8. Here, however, there is a seventh line which is dotted and unidentified. This line represents the dew point of the "as generated" line and should be read against the right-hand side ordinate of the dew point. It goes from dew point of $80^\circ F$ to a dew point of about $138^\circ F$.

While in the preceding disclosure we have specifically described four different specific embodiments of the present invention, it will be appreciated that there are a wide number of metallurgical and chemical processes carried out in oxygen bearing gaseous atmospheres wherein the method and apparatus made available by the present invention will be applicable. Accordingly, it will be appreciated that the invention makes available a new and improved control method and apparatus for controlling the processing of products in oxygen bearing gaseous atmospheres by determining the ability of the oxygen in the gas phase to chemically affect the product through reduction, oxidation, carburization or some other comparable phenomenon, and thereafter employ this determination in the further control of the conditioning of the gaseous atmosphere in order to optimize its processing capabilities.

WHAT WE CLAIM IS:—

1. A control apparatus for controlling processing of a product in a controllable processing vessel having a gaseous atmosphere containing oxygen, characterised by comprising a source of process control gas, control means for controlling the supply of process control gas from said source to the processing vessel, a gas analyzer measuring means of the type capable of obtaining a measurement of the equilibrium oxygen partial pressure of the gaseous atmosphere in the vessel to thereby provide an indication of the oxygen potential of the gaseous atmosphere, and deriving an output measurement signal indicative of the oxygen potential, and feedback and control means for effectively applying said output measurement signal back to control the operation of the control means for controlling the supply of process control gas to the processing vessel for optimizing the process.

2. A control apparatus according to claim 1 wherein the product being processed is a metal product being either reduced or oxidized and the equilibrium oxygen partial pressure at which the metal begins to reduce or oxidize is given by the expression:

$$pO^0_{M_aO_b} = \frac{(\Delta G^0_{M_aO_b})/b}{4.575T}$$

where

$\Delta G_{\text{MaOb}}^{\circ}$ = Gibbs free energy of formation of MaOb (Cal/mole)

MaOb = the stoichiometric oxide formula

5 b = a stoichiometric coefficient for the oxide reaction

T = temperature ($^{\circ}$ Kelvin)

3. A control apparatus according to claim

2 wherein the process is one for oxidizing a metal product and the control gas flow is regulated so that

$$pO < pO_{\text{MaOb}}^{\circ}$$

at processing temperatures at which the kinetics of the reaction does not limit the rate of formation of the oxide and at which pO is a logarithmic expression of the oxygen partial pressure derived from the measured oxygen partial pressure pO₂ by the equation

$$20 \quad pO = \log \left(\frac{1}{[pO_2]^{1/2}} \right)$$

4. A control apparatus according to claim 2 wherein the process is one for reducing a metal oxide and the control gas flow rate is regulated so that

$$25 \quad pO > pO_{\text{MaOb}}^{\circ}$$

at processing temperatures at which the kinetics of the reaction does not limit the rate of the reduction and where pO is a logarithmic expression of the oxygen partial pressure derived from the measured oxygen partial pressure PO₂ by the equation

$$30 \quad pO = \log \left(\frac{1}{[pO_2]^{1/2}} \right)$$

5. A control apparatus according to claim 2 wherein the product being processed is a metal product being annealed in a controllable annealing furnace and the equilibrium oxygen partial pressure at which the metal begins to oxidize is given by the expression

$$pO_{\text{MaOb}}^{\circ} = - \frac{\Delta G_{\text{MaOb/b}}^{\circ}}{2.303 RT}$$

40 where

$\Delta G_{\text{MaOb}}^{\circ}$ = Gibbs free energy of formation of MaOb (Cal/mole)

MaOb = the stoichiometric oxide formula

45 b = a stoichiometric coefficient for the oxide reaction

R = gas constant (1.98718)

T = annealing temperature ($^{\circ}$ Kelvin)

6. A control apparatus according to claim

5 wherein the process control gas flow rate is regulated so that

$$pO > pO_{\text{MaOb}}^{\circ}$$

at processing temperatures where reaction kinetics are not rate limiting the oxide formation and where pO is a logarithmic expression of the oxygen partial pressure derived from the measured oxygen partial pressure pO₂ by the equation

$$pO = \log \left(\frac{1}{[pO_2]^{1/2}} \right)$$

7. A control apparatus according to claim 6 wherein the oxygen partial pressure measuring means senses the equilibrium oxygen partial pressure at a number of points along the length of the annealing furnace, the control apparatus further includes temperature sensing means for deriving temperature measurements at a number of points in the annealing furnace, and the feedback and control means includes computation means for comparing the actual measured equilibrium oxygen partial pressure at the measured temperature to a desired pO_{MaOb}[°] and deriving output control signals for controlling operation of the process control gas control means to maintain the relation

$$pO > pO_{\text{MaOb}}^{\circ}$$

at processing temperatures where reaction kinetics are not rate limiting the oxide formation.

8. A control apparatus according to claim 4 wherein the processing vessel is a direct reduction vessel in which the oxygen extracted per unit of reducing gas determines the reduction rate and the process efficiency in accordance with the expression

$$\frac{pO_{\text{in}} - pO_{\text{out}}}{pO_{\text{in}} - pO_{\text{MaOb}}^{\circ}}$$

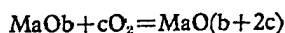
wherein pO_{in} and pO_{out} are the oxygen equilibrium partial pressures into and out of the source of process control gas, respectively, the process control gas control means includes flow rate measuring and control means for measuring and controlling the flow rate of the process control gas into and out of the direct reduction vessel, and the feedback and control means further includes computation means for deriving output controlling signals in accordance with the above expressions for controlling the oxygen potential and flow rate

of the process control gas to the direct reduction vessel.

9. A control apparatus according to claim 8 wherein the direct reduction vessel is of the counter-current type having means for recirculating process control gas through the vessel counter to the flow of the oxide materials being processed, the source of control gas comprises a gas regenerator having supplied thereto as inputs at least part of the recirculated process control gas from the vessel and a source of fresh primary gas and having the output thereof supplied to the vessel, the gas analyzer measures the oxygen partial pressure of the output control gas (pO_{out}) supplied from the gas regenerator to the vessel and the portion of the recirculated control gas (pO_{in}) supplied from the vessel to the gas generator, and the flow rate measuring and control means measures and controls the flow of fresh primary gas supplied to the gas regenerator.

10. A control apparatus according to claim 9 further including means for sensing the temperature at which the direct reduction vessel operates and for supplying the sensed temperature to the computation means as an input parameter for use in controlling the temperature at which the direct reduction vessel operates, and production rate monitoring means for measuring the output product of the reduction process and supplying the measurement to the computation means for cross checking the efficiency and operation of the system.

11. A control apparatus according to claim 3 wherein the processing vessel is a sintering furnace for selectively producing one of several polymorphic oxide species where the desired oxide $MaOb$ is related to undesired oxide species by the expression



the process control gas control means includes flow rate measuring and control means for measuring and controlling the flow rate of the process control gas into and out of the sintering furnace, and wherein the feedback and control means includes computation means for processing the input measurements and maintaining the flow rate and pO of the process control gas in a manner to satisfy the relation

$$pO^*_{MaOb} > pO > pO^*_{MaO(b+2c)}$$

12. A control apparatus according to claim 11 wherein the sintering furnace is of the recirculating type having at least a portion of the process control gas recirculated there-through and the source of control gas comprises a gas regenerator having the recirculated portion of the process control gas and fresh primary gas supplied thereto as inputs

with its output supplying the sintering furnace, the gas analyzer measures the oxygen partial pressure of the portion of the recirculated control gas and the output control gas from the gas regenerator, respectively, and the flow rate measuring and control means measures and controls the flow of fresh primary gas supplied to the gas regenerator.

13. A control apparatus according to claim 3 wherein the processing vessel is a carburizing furnace, the source of process control gas is a gas generator for burning a hydrocarbon fuel and supplying the products of combustion to the carburizing furnace, the gas analyzer means derives output measurement signals indicative of the oxygen partial pressure of the products of combustion supplied from the gas generator to the carburizing furnace as a control gas as well as the oxygen partial pressure of the gaseous atmosphere in the carburizing furnace, and the feedback and control means includes computation means for processing the measurement signals from the gas analyzer means and maintaining the carburizing atmosphere of the carburizing furnace in a condition to satisfy the relation

$$pO > pO^*_{MaOb}$$

14. A control apparatus according to claim 13 further including conditioning means for conditioning the products of combustion from the gas generator prior to supplying such to the carburizing furnace, the conditioning means comprising gas drying means and gas scrubbing means in series together with suitable dryer and scrubber control means for controlling the operation thereof, said gas analyzer means further including means for deriving measurement signals indicative of the oxygen partial pressure of conditioned process control gas at the outputs of the gas drying means and the gas scrubbing means, and means for supplying such measurement signals to the computation means for use in deriving control output signals for controlling the operation of the gas drying means and the gas scrubbing means.

15. A control apparatus according to claim 14 wherein the process control gas control means includes flow rate measuring and control means for measuring and controlling the air/fuel ratio of the gas generator, and processing temperature sensing and temperature control means coupled to the carburizing furnace for sensing and controlling the temperature of the furnace, each of said flow rate measuring and control means and said temperature sensing and temperature control means having their output signals coupled to and being controlled by the computation means.

16. A control apparatus according to claim 1 wherein the gas analyzer is of the type em-

ploying a solid oxygen-ion electrolyte, disposed between two electrodes with a reference gas having a known oxygen partial pressure being applied to one side of the electrolyte and the gas to be measured being applied to the remaining side.

17. A control method for controlling processing of a product in a controllable processing vessel having a gaseous atmosphere containing oxygen, characterized by controlling the supply of process control gas to the processing vessel, obtaining a measurement of the equilibrium oxygen partial pressure of the gaseous atmosphere in the processing vessel to thereby provide an indication of the oxygen potential of the gaseous atmosphere in the vessel and deriving an output measurement signal indicative of the oxygen potential, and applying said output measurement signal back to control the supply of process control gas to the processing vessel for optimizing the process being carried out therein.

18. A control method according to claim 17 wherein the oxygen potential of the gaseous atmosphere in the processing vessel is directly sensed by means of a gas analyzer of the type capable of directly obtaining a measurement of the equilibrium oxygen partial pressure of the gaseous atmosphere in the vessel to thereby provide an indication of the oxygen potential of the gaseous atmosphere.

19. A control method according to claim 18 wherein the product being processed is a metal product being either reduced or oxidized and the equilibrium oxygen partial pressure at which the metal begins to reduce or oxidize is given by the expression

$$pO^*_{MaOb} = -\frac{\Delta G^*_{MaOb/b}}{4.575 T}$$

where

ΔG^*_{MaOb} = Gibbs free energy of formation of $MaOb$ (Cal/mole)

$MaOb$ = the stoichiometric oxide formula
b = a stoichiometric coefficient for the oxide reaction

T = temperature ($^{\circ}$ Kelvin).

20. A control method according to claim 19 wherein the process is one for oxidizing a metal product and the control gas flow rate is regulated so that

$$pO < pO^*_{MaOb}$$

at processing temperatures where reaction kinetics are not rate limiting the oxide formation, and where pO is a logarithmic expression of the oxygen partial pressure derived

from the measured oxygen partial pressure pO_2 by the equation

$$pO = \log \left(\frac{1}{[pO_2]^{1/2}} \right)$$

21. A control method according to claim 20 wherein the process is one for reducing a metal oxide and the control gas flow rate is regulated so that

$$pO > pO^*_{MaOb}$$

at processing temperatures where reaction kinetics are not rate limiting the reduction and where pO is a logarithmic expression of the oxygen partial pressure derived from the measured oxygen partial pressure pO_2 by the equation

$$pO = \log \left(\frac{1}{[pO_2]^{1/2}} \right)$$

22. A control method according to claim 18 wherein the product being processed is a metal product being annealed in a controllable annealing furnace and the equilibrium oxygen partial pressure at which the metal begins to oxidize is given by the expression

$$pO^*_{MaOb} = -\frac{\Delta G^*_{MaOb/b}}{2.303 RT}$$

where

ΔG^*_{MaOb} = Gibbs free energy of formation of $MaOb$ (Cal/mole)

$MaOb$ = the stoichiometric oxide formula
b = a stoichiometric coefficient for the oxide reaction

R = gas constant (1.98718)

T = annealing temperature ($^{\circ}$ Kelvin)

23. A control method according to claim 22 wherein the process control gas flow rate is regulated so that

$$pO > pO^*_{MaOb}$$

at processing temperatures where reaction kinetics are not rate limiting the oxide formation and where pO is a logarithmic expression of the oxygen partial pressure derived from the measured oxygen partial pressure pO_2 by the equation

$$pO = \log \left(\frac{1}{[PO_2]^{1/2}} \right)$$

24. A control method according to claim 23 further comprising measuring the equilibrium oxygen partial pressure at a number of points along the length of the annealing furnace, measuring the temperature at a number of points in the annealing furnace, and comparing the actual measured equilibrium oxygen partial pressures and the actual measured temperature to a desired pO_{MaOb}^* and temperature at the point in question and deriving control signals for controlling the flow of process control gas and temperature of the furnace so as to maintain the relation

$$pO > pO_{MaOb}^*$$

at processing temperatures where reaction kinetics are not rate limiting the oxide formation.

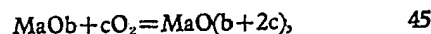
25. A control method according to claim 21 wherein the processing takes place in a direct reduction vessel in which the oxygen extracted per unit of reducing gas determines the reduction rate and the process efficiency in accordance with the expression

$$\frac{pO_{in} - pO_{out}}{pO_{in} - pO_{MaOb}^*}$$

where pO_{in} and pO_{out} are the oxygen equilibrium partial pressures into and out of the source of process control gas, respectively, and the process further includes measuring and controlling the flow rate of the process control gas from the source into and out of the direct reduction vessel, and deriving output controlling signals in accordance with the above expression for controlling the oxygen potential by varying the flow rate of the process control gas from the source into and out of the direct reduction vessel to optimize the reduction process.

26. A control apparatus according to claim 20 wherein the processing vessel is a sinter-

ing furnace for selectively producing one of several polymorphic oxide species where the desired oxide $MaOb$ is related to undesired oxide species by the expression



and the process further includes measuring and controlling the flow rate of the process control gas into and out of the sintering furnace, and processing the input measurements to derive output control signals for maintaining the flow rate and pO of the process control gas in a manner to satisfy the relation

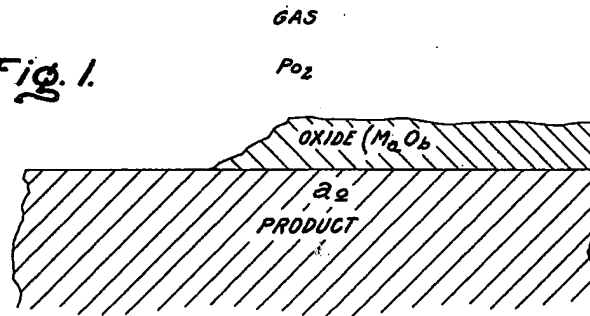
$$pO_{MaOb}^* > pO > pO_{MaO(b+2c)}^*$$

27. A control apparatus according to claim 20 wherein the processing vessel is a carburizing furnace and the process control gas is obtained by burning a hydrocarbon fuel in a gas generator and supplying the products of combustion to the carburizing furnace, conditioning the products of combustion from the gas generator prior to supplying such to the carburizing furnace, directly deriving output measurement signals indicative of the oxygen partial pressure of the conditioned process control gas at each conditioning stage, the oxygen partial pressure at the output of the gas generator and the oxygen partial pressure of the atmosphere in the carburizing furnace, measuring and controlling the air/fuel ratio of the gas generator, sensing and controlling the temperature of the furnace, and controlling the gas generation, gas conditioning, gas flow rate and temperature of the furnace in accordance with oxygen partial pressure measurements to thereby optimize the carburization process.

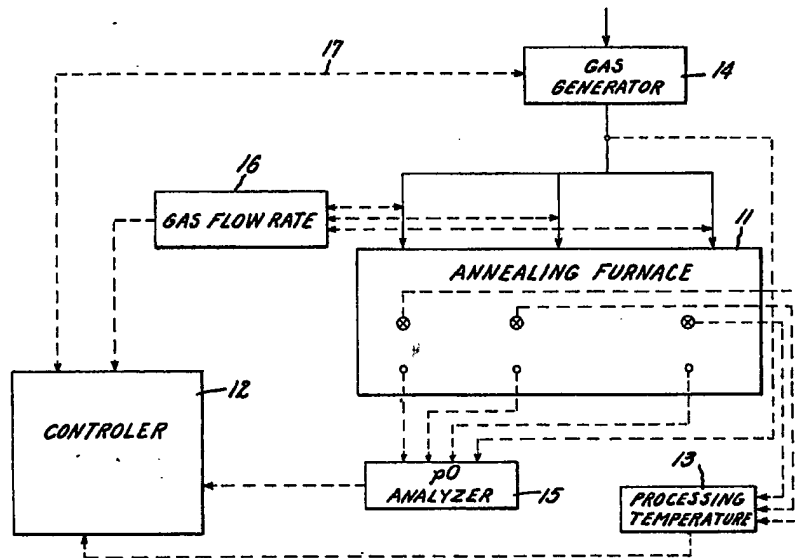
28. A control apparatus substantially as described with reference to and as illustrated in the accompanying drawings.

29. A control method as claimed in claim 17, substantially as hereinbefore described.

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Fig. 1.*Fig. 2.*

PROTECTIVE ATMOSPHERE CONTROL



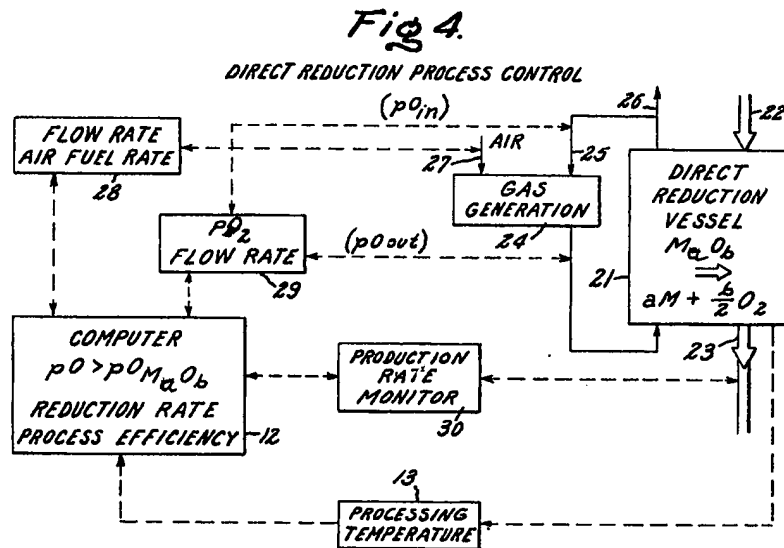
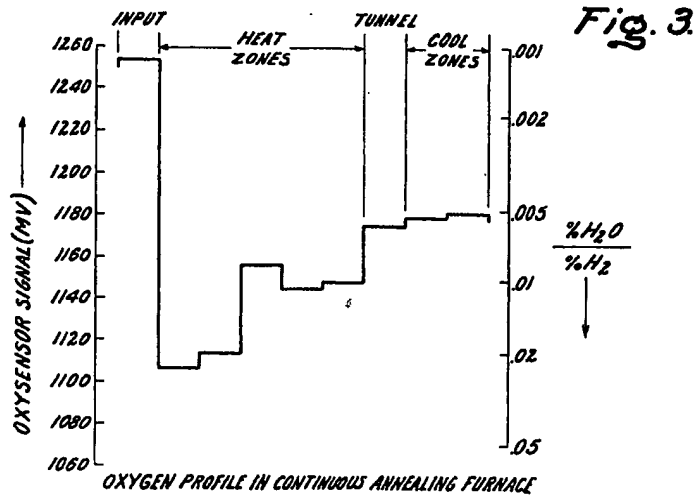


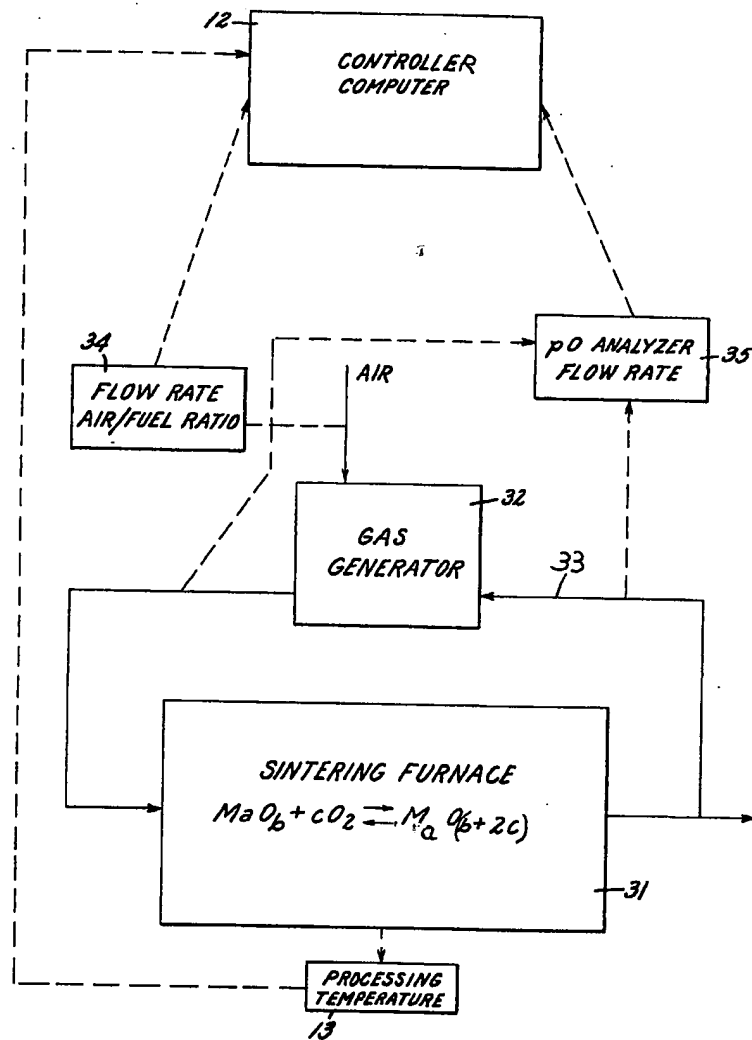
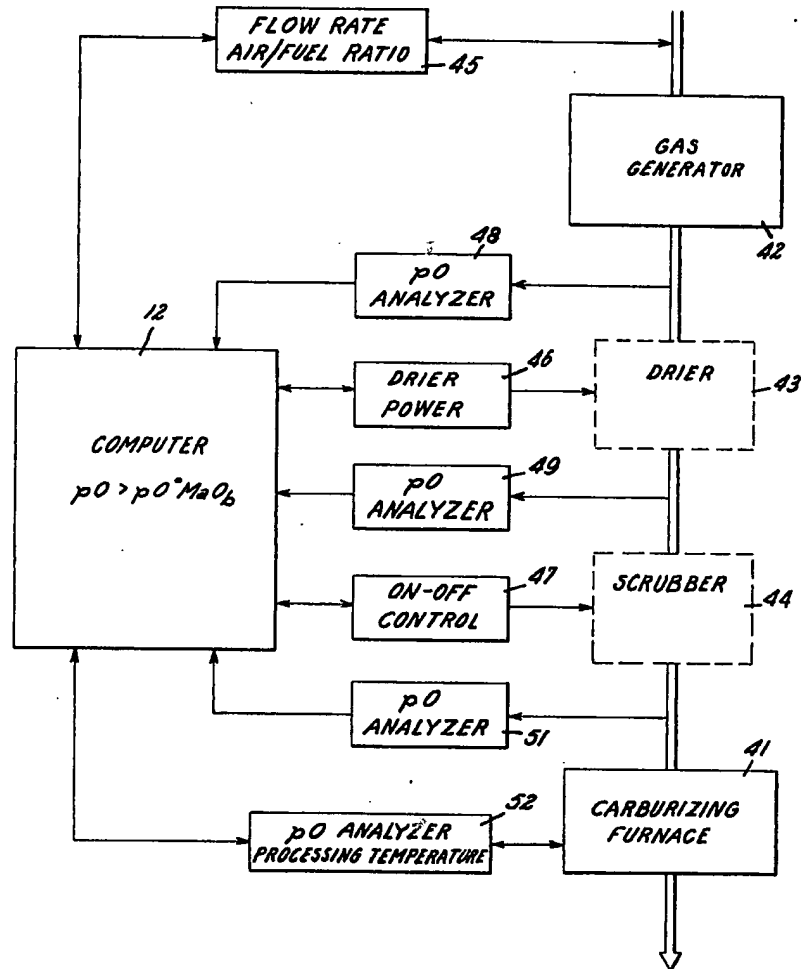
Fig. 5.**SINTERING ATMOSPHERE CONTROL**

Fig. 6.

CARBURIZING ATMOSPHERE CONTROL



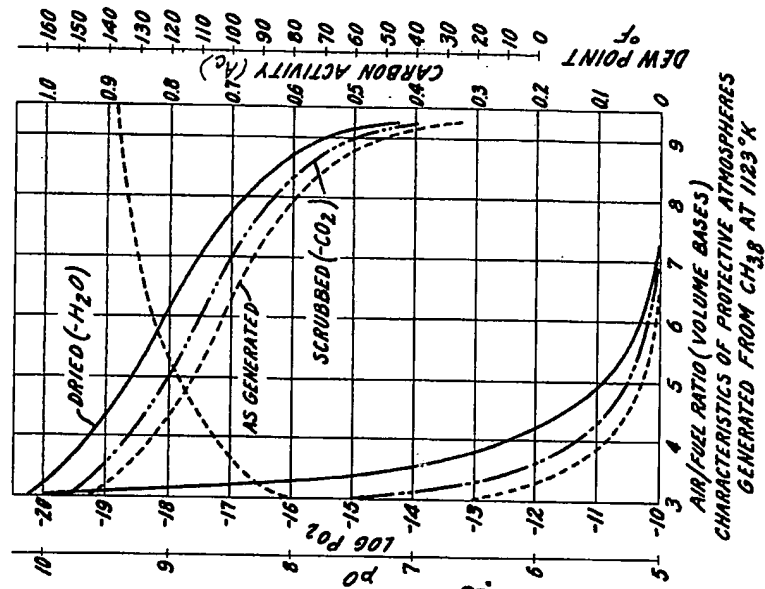


Fig. 8.

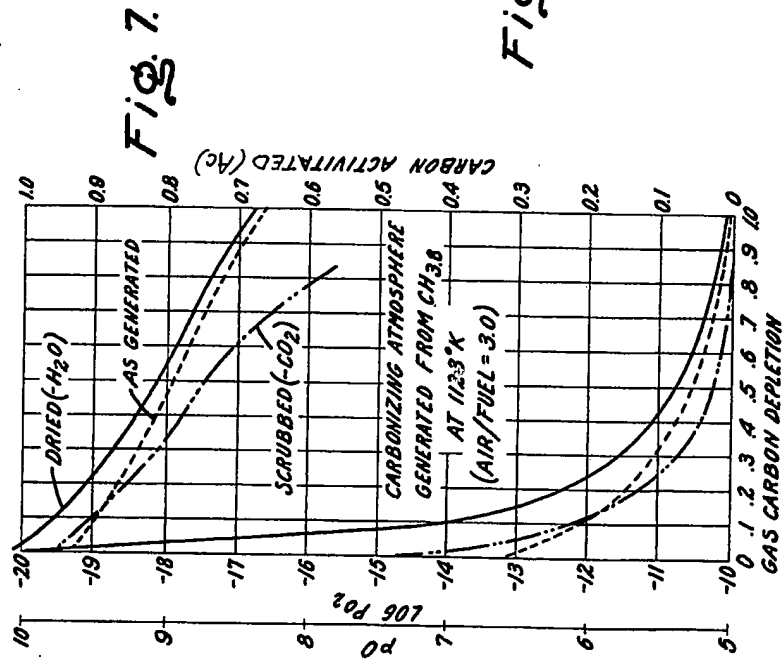


Fig. 7.